A NEW MODEL OF KEROGEN STRUCTURE
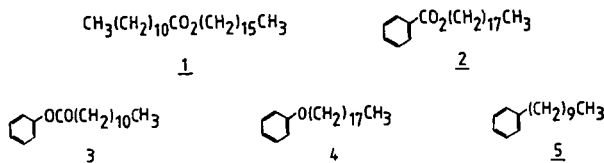
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INTRODUCTION

By far the most prominent components of a typical shale oil are n-alkanes and n-alkenes, which form a homologous series extending to C_{30} or beyond. Since it is now clear that these molecules are readily converted into aromatics and branched aliphatics under retorting conditions[1], it is likely that n-alkanes and n-alkenes are the major primary products of kerogen pyrolysis. Knowledge of how they are generated is thus of crucial importance to oil shale chemistry, particularly with respect to the nature of kerogen.

Although the literature abounds with proposals for the structure of kerogen, most are based on the results of oxidative degradations[2]. Although these experiments provide useful information about individual structural fragments, very little can be learned about the way in which they are linked, since virtually all functional groups are converted into carboxylic acids. Nevertheless, it is generally accepted that kerogen is composed of both aliphatic and aromatic structures, with the most convincing evidence for the latter coming from solid-state ^{13}C nuclear magnetic resonance (NMR) and infrared studies of intact kerogens and shales.

We have made the assumption that the aromatic and aliphatic moieties are associated, and that kerogen consists mainly of n-alkyl chains attached to a largely involatile aromatic (or more likely heteroaromatic) nucleus. On pyrolysis, the aliphatic side chains are cleaved to form oil, whereas most of the hydrogen-deficient nucleus forms coke. To test this hypothesis, we have pyrolysed a range of appropriate model compounds, 1 - 5, and compared the products and kinetics of their decomposition with data obtained from oil shales.

$$CH_3(CH_2)_{10}CO_2(CH_2)_{15}CH_3 \qquad \bigcirc\!\!-CO_2(CH_2)_{17}CH_3$$

<u>1</u>   <u>2</u>

$$\bigcirc\!\!-OCO(CH_2)_{10}CH_3 \qquad \bigcirc\!\!-O(CH_2)_{17}CH_3 \qquad \bigcirc\!\!-(CH_2)_9CH_3$$

<u>3</u>   <u>4</u>   <u>5</u>

EXPERIMENTAL

Pyrolyses were carried out in a quartz flow tube enclosed in the oven of a gas chromatograph. The compounds were transferred in a stream of helium from an evaporation chamber held at a temperature (usually around 200°C) sufficient to give a partial pressure of reactant of approximately 150 Pa. The products were collected in U-tubes immersed in liquid nitrogen and analysed by ^1H NMR using a JEOL GX400 spectrometer. For each compound, the residence time was constant but the reactor temperature was varied to give between 5 and 50% decomposition.

Activation energies were then calculated from a plot of log x v. $1/T$, where x is the fraction decomposed at temperature T (in K). Rate constants (k) were calculated from the formula $kt = \ell n(1-x)$. Solid state ^{13}C spectroscopy was performed on a Bruker CXP300 instrument, using the Dixon total side-band suppression sequence(3).

RESULTS AND DISCUSSION

Support for the presence of n-alkyl chains is gained from the high field solid-state ^{13}C NMR spectrum of a Condor carbonaceous kerogen (Figure 1, upper trace). The lower trace is the solution spectrum of a carbonaceous shale oil for comparison. Particularly noteworthy is the correspondence of signals A and D between the two spectra, which shows that long n-alkyl chains, free at one (or each) end, are present in the kerogen.

Information about the site of attachment of these chains was provided by ^{13}C NMR examination of the alkene fraction isolated from a Condor oil. Although the occurrence of 1-enes in shale oils is well documented, there is very little information on the distribution of other double-bond isomers. Figure 2 shows that high field ^{13}C NMR is an excellent method for determining this distribution, at least for the first five or six carbons along the chain, giving cis/trans ratios as well.

The quantitative data from this spectrum were best interpreted as indicating that 1-enes are in fact the initially-formed olefins and that the double bond then migrates along the chain.* Thus the terminal carbon is the likely site of their original linkage to the kerogen. This is consistent with the widespread occurrence in the biosphere of long-chain fatty acids and, to a lesser extent, primary alcohols and their isolation from the hydrolysis of kerogens(4). We have therefore based the following models on these two classes of compounds and used the benzene ring as the simplest aromatic nucleus.

Hexadecyl dodecanoate - 1. This wax ester pyrolysed readily between 430 and 460°C to give almost exclusively 1-hexadecene and dodecanoic acid. Significantly, very little n-undecane was formed. The reaction was shown to be first order by varying the partial pressure of substrate between 40 and 600 Pa; except at the lowest concentration, no significant change in the fractional decomposition at 450°C was observed. The calculated activation energy and rate constant at 450°C are given in Table 1, together with the corresponding parameters for the evolution of hydrocarbons by pyrolysis of several oil shales. As can be seen, neither the kinetics nor the products of this reaction correspond well with those from oil shales.

Octadecyl benzoate - 2. This ester decomposed even more readily than the previous compound, giving 1-octadecene and benzoic acid as almost the only products. However, a small amount of benzene was also formed, presumably from decarboxylation of the benzoic acid. Thus, this compound cannot be considered a good kerogen model.

Phenyl dodecanoate - 3. Phenolic esters of fatty acids have been implicated in the structure of humic substances(9) such as those derived from lignins. It was therefore interesting to discover that although phenyl dodecanoate pyrolysed rather slowly, the activation energy for its decomposition is similar to that

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* dehydrogenation of alkanes is an additional pathway(1), leading to a significant proportion of olefins with a random distribution of double-bond positions.

for Nagoorin carbonaceous shale, which contains large quantities of lignitic materials. Furthermore, the major products derived from the side chain were n-undecane and 1-decene (Figure 3). Pyrolysis of phenolic esters of a natural series of carboxylic acids, where even numbered chains predominate, should therefore generate n-alkanes with odd over even preference and 1-enea with a less pronounced even over odd preference. This is often observed in shale oils.

Phenyl octadecyl ether - 4. The decomposition kinetics of this compound were complicated. Above about 460°C, the reaction appeared to have an activation energy of less than 200 kJ mol^{-1}, whereas at lower temperatures the value was more than 500 kJ mol^{-1}. This probably indicates that the initial bond-cleavage is not the rate-determining step below 460°C, but it may be above this temperature. The products were even more complex; their chromatogram is shown in Figure 4.

Note the homologous series of n-alkanes dominated by heptadecane, and the more abundant series of 1-enes, with 1-octadecene the major compound. Phenol and, unexpectedly, benzaldehyde are the major aromatic products, although styrene and various alkylbenzenes including n-heptadecylbenzene were also identified. In addition, products arising from the random scission of the side chain of 4 are present in significant amounts.

Although the products and rate of decomposition of this compound correspond well to those of oil shales, the complicated activation energy precludes a decision about its validity as a kerogen model.

Decylbenzene - 5. This compound, which represents the simplest linkage of an alkyl chain to an aromatic ring, pyrolysed extremely slowly, although its activation energy was virtually identical to those reported for the decomposition of typical oil shales. The major products were styrene, toluene, ethylbenzene and 1-nonene; only very small amounts of n-alkanes were detected. As with the previous compound, there was also cleavage of carbon-carbon bonds along the side chain.

CONCLUSIONS

Of the five compounds pyrolysed in this study, only phenyl dodecanoate can be considered as a good model of kerogen structure, but only for the carbonaceous shales. None of the other compounds, with the possible exception of phenyl octadecyl ether, adequately mimicked either the high or low activation energy processes of oil shale pyrolyses.

The nature of the higher activation energy process is rather intriguing. The fact that roughly equal quantities of n-alkanes and alkenes are generated by the rapid pyrolysis of shales and kerogens suggests that the two classes of compounds have a common origin; indeed kinetic data(7,8) indicate that a single rate-determining process is involved in the formation of the bulk of the oil. We believe that this process involves the generation of primary n-alkyl radicals which would then disproportionate to give equal quantities of n-alkanes and 1-alkenes. Certainly, other have provided evidence for the involvement of radicals in kerogen pyrolysis(10). However, the reaction which produces these radicals has yet to be elucidated.

ACKNOWLEDGEMENTS

for the use of a least-squares analysis program, and Dr. J.K. Saunders (University of New South Wales) for assistance in determining the solid-state NMR spectrum. We are also grateful to Dr. A. Ekstrom for helpful discussions and permission to quote unpublished data.

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TABLE 1
ACTIVATION ENERGIES AND RATE CONSTANTS AT 450°C FOR THE DECOMPOSITION OF MODEL COMPOUNDS AND GENERATION OF OIL FROM SHALES

| Substance	Activation Energy kJ mol^{-1} ($\pm$ 1 σ)	Rate Constant (450°C) s^{-1}
Hexadecyl dodecanoate	172 ± 2	1.78 x 10^{-2}
Octadecyl benzoate	163 ● 2	2.21 x 10^{-2}
Phenyl dodecanoate	147 ● 7	1.60 x 10^{-3}
Phenyl octadecyl ether	see text	4.26 x 10^{-3}
Decylbenzene	222 ± 5	4.45 x 10^{-5}
Green River shale (5)	219	3.95 x 10^{-3}
Rundle shale		5.8 x 10^{-3} (6)
Rundle kerogen		7.7 x 10^{-3} (6)
Condor shale (7)	232	1.73 x 10^{-3}
Nagoorin carbonaceous shale (8)	152	5.22 x 10^{-3}
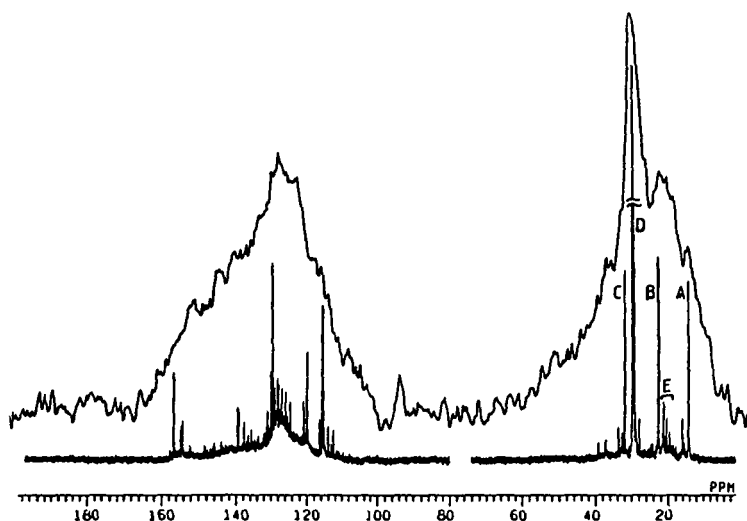
FIGURE 1: (Upper trace) 75 MHz CPMAS ^{13}C NMR spectrum of a Condor carbonaceous kerogen. (Lower trace) solution ^{13}C spectrum of a carbonaceous shale oil showing signals due to A, terminal methyls (C-1); B, C-2; C, C-3; and D, C-4+ of n-alkyl chains, and E, aromatic methyls. Most of the sharp lines in the aromatic region (110-160 ppm) are from phenols.
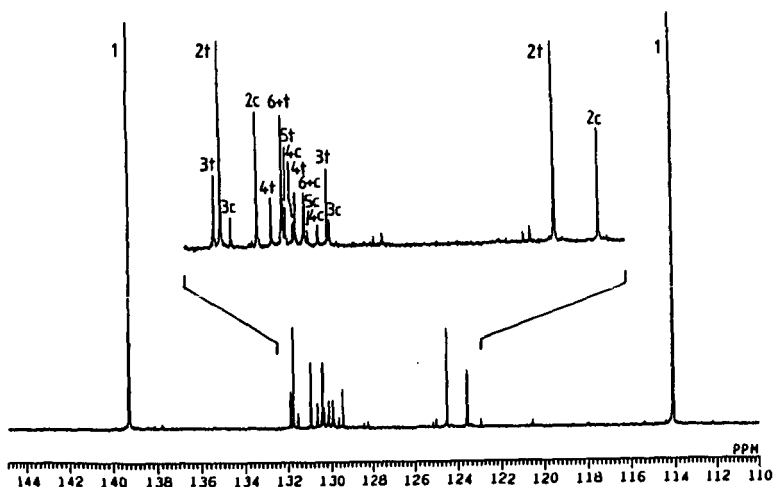
FIGURE 2: Olefinic region of 100 MHz ^{13}C NMR spectrum of the alkene fraction from Condor shale oil. The label 2t (for example) refers to signals from straight chain trans-2-enes.

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FIGURE 3: Reconstructed ion chromatogram of products from the decomposition of phenyl dodecanoate: ● = n-alkanes, o = 1-alkenes.
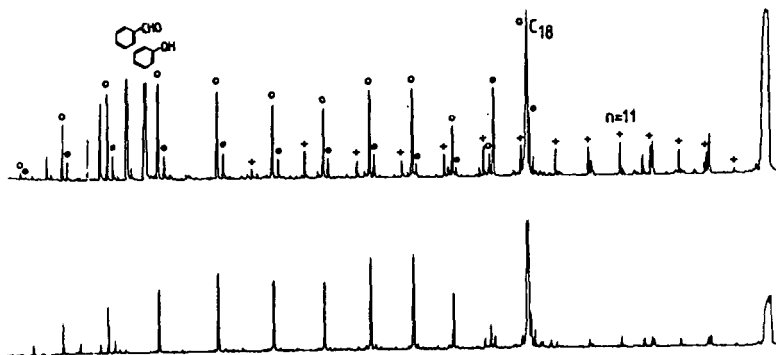
FIGURE 4: Reconstructed ion chromatogram of products from the decomposition of phenyl octadecyl ether; + = $C_6H_5O(CH_2)_nCH=CH_2$.